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Lattice variation and thermal parameters of KDP crystals added with NaCl and NaBr

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Abstract : Pure and impurity-added (with NaCl and NaBr) KDP (potassium dihydrogen orthophosphate) single crystals were grown by the slow evaporation method from aqueous solutions. X-Ray diffraction data were collected for powder samples and used for the estimation of lattice variation and thermal parameters like Debye-Waller factor, mean-square amplitude of vibration, Debye temperature and Debye frequency. The thermal parameters do not vary in a particular order with respect to impurity concentration. The results obtained are reported.

Keywords : Impurity-added KDP crystals, X-ray diffraction, lattice parameters, thermal parameters.

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1. Introduction

Potassium dihydrogen orthophosphate, KH_2PO_4 (KDP), has a tetramolecular unit cell having the dimensions [1] given as $a = b = 7.448$ Å and $c = 6.977$ Å. Several research workers have shown considerable interest on it due to its importance. Pure and impurity added KDP single crystals were grown from aqueous solutions and also in gel media and characterized by different workers [2–5]. KDP crystal continues to be an interesting material both academically and industrially.

Impurities are present in all crystallization processes. Usually, impurities are adventitious and undesirable but sometimes they are intentionally added and then they are called additives. The effect of impurities on the growth rate and habit of KDP crystal growing in solution, has been the subject of many experimental and theoretical studies over many years. In most of them, it was reported [6–21] that impurities cause inhibitions in crystal growth and this effect was explained by the adsorption processes at different sites on the growing surface. A contrary effect involving an increase in the growth rate of crystal faces in the presence of low concentrations of additives, is also reported [6, 7, 9, 13–17, 19–21]. Such a growth-promoting effect of additives, is also called the catalytic effect of additives [19, 21]. The effect is observed in the presence of organic [6, 7, 14–17, 19–21] as well as inorganic additives [13, 20].

Similarly, some interesting results have been reported on the electrical properties of impurity added KDP single crystals. Some impurities have increased the electrical conductivity [22–26] and few others have decreased the same [27]. To explain the effect of impurities, one needs experimental data for diverse additives for various properties. This prompted a research programme to be carried out in this laboratory on the growth and physical properties of pure and impurity (various types) added KDP single crystals.

It is a known fact that NaCl and NaBr are model ionic substances and they exist as single ions in the crystals. So, if they are added as impurity to KDP, the halide ions are also expected to move (in all directions) along with protonic movement [24] which may create a complex situation on the electrical and thermal properties of KDP crystals. A systematic study in this direction may be useful in understanding the effect of NaCl and NaBr as impurities, on the electrical and thermal properties

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of KDP single crystals. Results of growth, density measurement, estimation of impurity concentration, D.C. electrical conductivity measurement, *etc.* have already been reported [27]. Herein, we report the results of our X-ray diffraction measurement (determination of lattice and thermal parameters) on KDP added with NaCl and NaBr.

2. Experimental details

Pure and impurity-added single crystals were grown by the slow evaporation method from aqueous solutions. KDP was added with NaCl and NaBr separately, each in six different KDP : impurity molecular ratios, *viz.* 1 : 0.000 (pure KDP), 1 : 0.002, 1 : 0.004, 1 : 0.006, 1 : 0.008 and 1 : 0.010. Impurity concentration in the crystal was also determined [27].

X-Ray diffraction data were collected from powder samples of crystals using an automated X-ray diffractometer with monochromated CuK_α radiation (λ = 1.5418 Å) and scintillation counter (scan speed 2°/min) at a temperature of 25 ± 1°C (2θ range : 10 to 90°). The reflections were indexed following the procedures of Lipson and Steeple [28]. Processing of the raw intensity data was done following the procedures of Warren [29]. Lattice parameters were determined from the indexed data using high angle reflections within an accuracy of ± 0.020. Lattice parameters together with volume (V) values and estimated impurity concentration [27] are presented in Table 1.

The mean Debye-Waller factors were determined by the Wilson plot method [30]. For the calculation of structure factors, the atomic scattering factors were taken from the literature [31, 32].

Table 1. Lattice parameters and estimated impurity concentrations.

System (impurity in mole %)	Estimated impurity concentration (mole %)	Lattice parameters		
		a(Å)	c(Å)	V(Å^3)
Pure KDP	–	7.453	6.984	387.9
NaCl added KDP				
0.2	0.075	7.480	6.974	390.2
0.4	0.161	7.565	6.857	392.4
0.6	0.247	7.321	7.375	395.3
0.8	0.333	7.330	7.407	398.0
1.0	0.419	7.394	7.324	400.4
NaBr added KDP				
0.2	0.125	7.480	6.975	390.3
0.4	0.276	7.566	6.857	392.5
0.6	0.427	7.332	7.395	397.5
0.8	0.579	7.330	7.438	399.7
1.0	0.730	7.395	7.324	400.5

In an actual X-ray diffraction experiment, one measures the intensities rather than the amplitudes of reflected beam. The intensity is directly proportional to the square of the amplitude $I_{hkl} \propto |F_{hkl}|^2$. In the present work, calculation of structure factor was done according to Warren [29].

As the entire crystal structure can be represented by the atomic array within one unit cell of the lattice, the contribution from atoms in one unit cell need be considered. When the amplitudes of the wavelets scattered by each atom in the unit cell are added, one obtains the structure factor (F).

KDP has the molecular formula KH_2PO_4. Each unit cell has 4 molecules. Hence, KDP has 4 K atoms, 8 H atoms, 4 P atoms and 16 O atoms per unit cell. Unit cell of the impurity added KDP crystal is expected to have p (4 impurity molecules) in addition to the 4 KDP molecules where p is the factor showing the impurity concentration in the crystal.

For pure KDP crystal, the structure factor is

$$F = 4f_K + 8f_H + 4f_P + 16f_O = F_{KDP}.$$

The density [27] and lattice parameters show qualitatively that the impurity molecules have entered into the KDP lattice. The estimated impurity concentration in the crystal (see Table 1) shows that the impurities are mainly occupying the interstitial positions. Moreover, the impurity concentrations considered in the present study are small (<1 mole %). So, for impurity-added KDP crystals, the impurity molecules are assumed to be added in the KDP lattice in the same amount (ratio) as estimated. Hence, for impurity-added KDP crystals, the structure factors are :

$$F = F_{KDP} + p(4f_{Na} + 4f_{Cl})$$

for NaCl added KDP crystals; and

$$F = F_{KDP} + p(4f_{Na} + 4f_{Br})$$

for NaBr added KDP crystals. p is having the values of impurity concentration (mole% × 10^{-2}, *i.e.* values provided in Table 1 multiplied by 10^{-2}).

The thermal parameters, *viz.* Debye-Waller factor (B), mean square amplitude of vibration ($\langle u^2 \rangle$), Debye temperature (θ_D) and Debye frequency (f_D) were determined by using the methods followed by Freeda and Mahadevan [33].

3. Results and discussion

For both the impurities considered in the present study, the observed variation of volume of KDP crystal caused

by the impurities indicates qualitatively that the impurities have entered into the lattice of KDP crystals. Moreover, it can be seen that the volume varies further with the increase in impurity concentration of the aqueous solution of KDP, used for the growth of crystals.

The values of B, $\langle u^2 \rangle$, θ_D and f_D are presented in Table 2. For both the impurities considered in the present

Table 2. Thermal parameters and ionic vibrational frequencies.

System (impurity in mole%)	B (Å^2)	$\langle u^2 \rangle$ (Å^2)	θ_D (K)	f_D (× 10^{12} s^{-1})	$1/\tau_0$ (× 10^{13} s^{-1})
Pure KDP	7.184	0.091	167.8	3.495	2.197
NaCl added KDP					
0.2	19.314	0.245	102.0	2.126	1.336
0.4	5.416	0.069	193.5	4.031	2.534
0.6	2.744	0.035	273.3	5.695	3.580
0.8	17.980	0.228	105.8	2.203	1.385
1.0	3.199	0.041	252.7	5.265	3.309
NaBr added KDP					
0.2	4.869	0.062	204.6	4.263	2.680
0.4	3.335	0.042	247.8	5.164	3.246
0.6	1.434	0.018	381.5	7.948	4.996
0.8	6.991	0.089	170.2	3.547	2.230
1.0	6.862	0.087	171.7	3.579	2.250

study, no particular order was observed in the case of thermal parameters obtained, *viz.* B, $\langle u^2 \rangle$, θ_D and f_D with respect to impurity concentration. This is similar to that observed for KDP added with NH_4Cl, NH_4NO_3, $NH_4H_2PO_4$, $(NH_4)_2SO_4$, urea and $NiSO_4.7H_2O$ [33, 34]. No comparison is made with other studies since there is no data available in the literature for the systems considered in the present study.

Variation of B-values with impurity addition observed in the case of KDP added with urea, $NiSO_4.7H_2O$, NH_4Cl, NH_4NO_3, $NH_4H_2PO_4$ and $(NH_4)_2SO_4$ [33, 34] is small when compared to that observed in the present study for KDP added with NaCl and NaBr. This may be due to the random motion of halide ions [27] in the case of KDP added with NaCl and NaBr.

Considering the lattice variation (not distorted significantly) and variation of thermal parameters with impurity concentration observed in the present study, it may be possible for us to conclude that the addition of sodium halide impurities does not distort the KDP lattice significantly but affects the thermal (lattice) vibration much in a random way.

The Debye frequencies observed in the present study lie in the infrared range and that for the pure KDP (3.495×10^{12} s^{-1} at 25°C) nearly coincides with the frequency of υ' mode (2.5×10^{12} s^{-1} at 27°C) [35] assigned to oscillation modes of protons. This is one order of magnitude lower than that obtained by O' Keeffe and Perrino (3×10^{13} s^{-1}) [35, 36] for the proton jump frequency.

The D.C. electrical conductivity is easily calculated [37] to be

$$\sigma = Ne^2a^2/(kT\tau),$$

where τ is a mean jump time, perhaps different from that for dipolar orientation but still given by an equation like

$$\frac{1}{\tau} = \frac{1}{\tau_o}\exp\left(\frac{-E}{kT}\right)$$

where a is the distance of a jump. The factor $1/\tau_0 = \omega_0$ (nearly equal to $2\pi f_D$) is the ionic vibrational frequency around its equilibrium position and exp $(-E/kT)$ is the statistical Boltzmann factor. A jump is attempted with each vibration, but only a fraction succeeds, depending on the (activation) energy E required in order to squeeze through the barrier to neighbouring equilibrium position. N stands for the number of perfect bonds or the number of charges per unit volume. The frequency $1/\tau_0 \approx 10^{13}$ s^{-1} [37].

$1/\tau_0$ values have been estimated using the f_D values and are presented in Table 2. The values of $1/\tau_0$ obtained in the present study, compare well with those expected by the model ($\approx 10^{13}$ s^{-1}). This shows that the values of thermal parameters determined in the present study for pure and sodium halide impurity-added KDP crystals, are reasonable and valid. Moreover, the ionic vibrational frequency observed for the pure KDP ($1/\tau_0 = 2.197 \times 10^{13}$ s^{-1}) nearly coincides with the oscillation frequency of the P-O-H group in orthophosphates (4×10^{13} s^{-1} [35]).

4. Conclusions

Pure and sodium halide impurity-added KDP single crystals were grown by the free evaporation method from aqueous solutions. Lattice and thermal parameters like Debye-Waller factor, mean square amplitude of vibration, Debye temperature and Debye frequency were determined from X-ray powder diffraction data. Variation of lattice volume with impurity concentration indicates qualitatively that the impurity molecules have entered into the KDP lattice. The obtained thermal parameters do not follow any particular order with respect to impurity concentration. The present study indicates that the addition of sodium halide impurities (NaCl and NaBr) does not distort the

KDP lattice significantly but affects the thermal (lattice) vibrations much in a random way. Estimation of ionic vibrational frequency around its equilibrium position using the Debye frequency, shows that the thermal parameters obtained in the present study, are reasonable and valid.

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